

**DEGRADATION OF HIGH DENSITY POLYETHYLENE CONTAINING
MANGANESE CARBOXYLATES AS PRO-DEGRADANT ADDITIVES UNDER
ARTIFICIAL AND NATURAL WEATHERING**

MARYUDI

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ABSTRACT

The tremendous utilization of synthetic plastics over last decades has led to environmental problems due to lack of degradability of plastics. The degradability issue has resulted in development of degradable plastics which degrade faster. This study deals with utilization of manganese carboxylates (i.e. manganese laurate, manganese palmitate and manganese stearate) on enhancing degradation of high density polyethylene (HDPE). Initially, manganese carboxylates were synthesized through two-steps reactions: (i) sodium carboxylates synthesis by reacting sodium hydroxide and carboxylic acids, (ii) manganese carboxylates synthesis by reacting manganese chloride and sodium carboxylates. Characterization of manganese carboxylates was then carried out. Incorporation of manganese carboxylates up to 1% (w/w) into HDPE resin was carried out using twin screw extruder followed by injection molding to produce specimens. Thermal treatment was performed at 70°C for maximum duration of 1000 hours to examine the degradation of pure HDPE and HDPE containing manganese carboxylates. Accelerated weathering was conducted up to 1000 hours combining thermal and UV exposure. Natural weathering was carried out for 24 weeks under weather conditions of Gambang, Malaysia. Analyses of tensile strength, elongation at break, FTIR spectra, average molecular weight, melt flow index (MFI), thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were carried out to assess the changes during treatments. Results have revealed that all manganese carboxylates have demonstrated adequate thermal stability. Their melting temperatures are in range of 108-117 °C. Manganese stearate has shown the highest thermal stability and melting point among manganese carboxylates synthesized. Thermal treatment has led to thermo-oxidative degradation of HDPE. Manganese carboxylates have significantly played a role in enhancing degradation of HDPE. The degradation increased by increasing amount of manganese carboxylates. During accelerated weathering, the degradation took place more rapidly than during thermal treatment, particularly for HDPE containing manganese carboxylates. Photo-degradation and thermo-oxidative degradation took place simultaneously during accelerated weathering and allowed dramatic reductions of essential properties. Natural weathering has given similar effects with accelerated weathering. Manganese carboxylates has also shown the capabilities on enhancing degradation of HDPE in natural environment. Manganese stearate has shown a slightly greater effect in enhancing degradation of HDPE than manganese laurate and manganese palmitate during all treatments. Pure HDPE lost its elongation at break about 16 %; 65 % and 64 %, whereas HDPE containing 1% manganese stearate lost its elongation at break about 62 %; 96 % and 95 % for thermal treatment; accelerated weathering and natural weathering respectively. Tensile strength and tensile modulus also decreased proportionally with the decrease of elongation at break. Other properties have also been found to decrease including average molecular weight, thermal stability, and melting point. The MFI, carbonyl index and crystallinity were found to increase after all treatments. Generally, manganese carboxylates have demonstrated the capabilities on enhancing degradation of HDPE under all modes of treatments.

ABSTRAK

Penggunaan bahan plastik yang banyak sejak beberapa dekad yang lalu membawa kepada masalah alam sekitar yang disebabkan oleh kekurangan sifat keteruraian bahan plastik. Isu keteruraian bahan plastik telah memberi kesan dalam pembaharuan penghasilan plastik yang lebih cepat terurai. Kajian ini melibatkan penggunaan mangan karboksilat (mangan laurat, mangan palmitat and mangan stearat) dalam meningkatkan penguraian polietilena ketumpatan tinggi (HDPE). Mangan karboksilat dihasilkan melalui dua kaedah tindakbalas: (i) natrium karboksilat disintesis melalui tindakbalas natrium hidroksida dengan asid karboksilik, (ii) mangan karboksilat disintesis melalui tindakbalas mangan klorida dengan natrium karboksilat. Pencirian mangan karboksilat kemudiannya dapat dihasilkan. Gabungan mangan karboksilat sehingga 1% (w/w) ke dalam HDPE resin telah dijalankan dengan menggunakan mesin pengestrud skru berkembar yang kemudiannya melalui suntikan acuan untuk menghasilkan spesimen. Rawatan terma dilakukan pada suhu 70°C dengan masa maksima iaitu selama 1000 jam dalam menguji tahap penguraian HDPE tulen dan HDPE yang mengandungi mangan karboksilat. Pecutan pencuciaan dijalankan sehingga 1000 jam yang menggabungkan pendedahan terhadap terma dan cahaya sinar UV. Pencuciaan semulajadi dilakukan selama 24 minggu dengan keadaan cuaca di kawasan Gambang, Malaysia. Analisa kekuatan tensil, pemanjangan pada takat putus, spektrum FTIR, purata berat molekul, indeks aliran leburan(MFI), termogravimetri(TG), pembezaan imbasan kalorimetri(DSC), pembelauan sinar-X(XRD), imbasan mikroskop elektron(SEM) telah dijalankan untuk menilai perubahan yang berlaku semasa perawatan. Hasil ujikaji telah mendedahkan semua mangan karboksilat menunjukkan kestabilan terma yang mencukupi. Suhu lebur bagi mangan karboksilat tersebut dalam lingkungan 108-117°C. Mangan stearat menunjukkan kestabilan terma yang tertinggi dan takat lebur di antara mangan karboksilat sintesis yang lain-lain. Rawatan terma telah menyebabkan penguraian oksidatif terma bagi HDPE. Mangan karboksilat merupakan bahan penting dalam meningkatkan tahap penguraian HDPE. Penguraian akan bertambah dengan pertambahan kuantiti bahan mangan karboksilat. Semasa pencuciaan pecutan, penguraian berlaku dengan lebih cepat berbanding semasa perawatan terma, terutama bagi HDPE yang mengandungi bahan mangan karboksilat. Penguraian foto dan penguraian oksidatif terma berlaku secara serentak semasa pencuciaan pecutan dan membenarkan berlakunya keretakan pada sifat-sifat penting secara dramatik. Pencuciaan semulajadi memberikan kesan serupa dengan pencuciaan pecutan. Mangan karboksilat juga menunjukkan kebolehpayaan dalam meningkatkan tahap penguraian HDPE di persekitaran semulajadi. Mangan stearat menunjukkan kesan yang lebih baik dalam meningkatkan tahap penguraian berbanding mangan laurat dan mangan palmitat dalam semua perawatan. HDPE tulen kehilangan pemanjangan pada takat putus iaitu 16%, 65% dan 64% sedangkan HDPE yang mengandungi mangan stearat kehilangan pemanjangan pada takat putus iaitu 65%, 96%, dan 95% bagi perawatan terma, pecutan pencuciaan dan pencuciaan semulajadi. Kekuatan tensil dan modulus tensil juga menurun secara berkadaran dengan penurunan pemanjangan pada takat putus. Sifat-sifat lain juga didapati merosot termasuk purata berat molekul, kestabilan terma dan takat lebur. Nilai MFI, indek karbonil dan sifat penkristalan didapati ada peningkatan dalam semua perawatan. Secara umumnya, mangan karboksilat telah menunjukkan keupayaan dalam meningkatkan penguraian HDPE dalam semua kedah perawatan.

TABLE OF CONTENTS

	Page
TITLE	i
SUPERVISOR’S DECLARATION	ii
STUDENT’S DECLARATION	iii
DEDICATIONS	iv
ACKNOWLEDGEMENTS	v
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	xiii
LIST OF FIGURES	xiv
LIST OF SYMBOLS	xix
LIST OF ABBREVIATIONS	xx
 CHAPTER 1 INTRODUCTION	
 1.1 RESEARCH BACKGROUND	1
1.2 PROBLEM STATEMENT	5
1.3 OBJECTIVES OF RESEARCH	6
1.4 SCOPE OF RESEARCH	6
1.5 CONTRIBUTIONS OF RESEARCH	7
 CHAPTER 2 LITERATURE REVIEW	
 2.1 INTRODUCTION TO PLASTICS	8
2.2 POLYETHYLENE	9
2.2.1 Classification of Polyethylene	11

2.2.2	Properties of Typical Polyethylene and Their Applications	13
2.3	PROCESSING METHOD OF PLASTICS	14
2.3.1	Compounding	15
2.3.2	Injection Molding	15
2.4	POLYETHYLENE PROPERTIES AND TESTING	16
2.4.1	Fourier Transform Infrared Spectroscopy	16
2.4.1.1	Fourier Transform Infrared Examination Techniques	17
2.4.1.2	Fourier Transform Infrared Spectra	19
2.4.2	Tensile Properties	20
2.4.3	Molecular Weight	22
2.4.3.1	Average Molecular Weight	23
2.4.3.2	Method of Average Molecular Weight Measurement	24
2.4.4	Melt Flow Index	28
2.4.5	Thermal Stability	29
2.4.5.1	Thermogravimetry Analysis	29
2.4.5.2	Experimental Aspects of Thermogravimetry Analysis	30
2.4.5.3	Interpretation of Thermogravimetry Curve	31
2.4.6	Melting Temperature	34
2.4.6.1	Factors That Influence Melting Temperature	35
2.4.6.2	Differential Scanning Calorimetry	36
2.4.6.3	DSC Scan Analysis	38
2.4.7	Crystallinity	40
2.4.7.1	Crystallinity of Polymer from DSC Scan	41
2.4.7.2	Crystallinity of Polymer from XRD Trace	41
2.4.8	Surface Morphology	45
2.4.8.1	Scanning Electron Microscope	45
2.4.8.2	Specimen Preparation	46
2.5	DEGRADATION OF PLASTICS	47
2.5.1	Thermo-Oxidative Degradation	48
2.5.2	Photo Degradation	51
2.5.3	Accelerated Weathering Degradation	55

2.5.4	Natural Weathering Degradation	56
2.6	ADDITIVES FOR DEGRADABLE PLASTICS	58
2.7	EVALUATION OF DEGRADATION	60
CHAPTER 3	METHODOLOGY	
3.1	OVERALL RESEARCH WORKS	62
3.2	MATERIALS	64
3.3	SYNTHESIS OF MANGANESE CARBOXYLATES	64
3.4	CHARACTERIZATION OF MANGANESE CARBOXYLATES	65
3.4.1	Free Fatty Acid Content	65
3.4.2	Bulk Density	65
3.4.3	Solubility	66
3.4.4	Water and Ash Contents	66
3.4.5	Degradation Temperature	66
3.4.6	Melting Temperature	66
3.5	COMPOUNDING	67
3.6	INJECTION MOLDING	67
3.7	TESTING	68
3.7.1	Carbonyl Index	68
3.7.2	Tensile Properties	68
3.7.3	Average Molecular Weight	69
3.7.4	Melt Flow Index	70
3.7.5	Degradation Temperature	70
3.7.6	Melting Temperature	70
3.7.7	Crystallinity	71
3.7.8	Surface Morphology	71

3.8	TREATMENTS	71
3.8.1	Thermal Treatment	71
3.8.2	Accelerated Weathering Treatment	72
3.8.3	Natural Weathering Treatment	72
3.9	DEGRADATION EVALUATION	72

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1	SYNTHESIS AND CHARACTERIZATION OF MANGANESE CARBOXYLATES	74
4.1.1	Synthesis of Manganese Carboxylates	74
4.1.2	Characterization of Manganese Carboxylates	75
4.2	THERMO-OXIDATIVE DEGRADATION OF HIGH DENSITY POLYETHYLENE	80
4.2.1	Introduction	80
4.2.2	Infrared Spectra	80
4.2.3	Tensile Properties	82
4.2.4	Molecular Weight	90
4.2.5	Melt Flow Index	92
4.2.6	Degradation Temperature	93
4.2.7	Melting Temperature and Crystallinity	96
4.2.8	Surface Morphology	98
4.3	DEGRADATION OF HIGH DENSITY POLYETHYLENE UNDER ACCELERATED WEATHERING TREATMENT	101
4.3.1	Introduction	101
4.3.2	Infrared Spectra	101
4.3.3	Tensile Properties	104
4.3.4	Molecular Weight	112
4.3.5	Melt Flow Index	114
4.3.6	Degradation Temperature	114

4.3.7	Melting Temperature and Crystallinity	118
4.3.8	Surface Morphology	121
4.4	DEGRADATION OF HIGH DENSITY POLYETHYLENE UNDER NATURAL WEATHERING	123
4.4.1	Introduction	123
4.4.2	Infrared Spectra	124
4.4.3	Tensile Properties	127
4.4.4	Molecular Weight	135
4.4.5	Melt Flow Index	136
4.4.6	Degradation Temperature	137
4.4.7	Melting Temperature and Crystallinity	139
4.4.8	Surface Morphology	143
4.5	COMPARATIVE EFFECT OF TREATMENTS	144
 CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS		
5.1	CONCLUSIONS	151
5.2	RECOMMENDATIONS	153
REFERENCES		154
 Appendix A		162
Appendix B		165
Appendix C		166

LIST OF TABLES

Table No.	Title	Page
2.1	Main properties of typical polyethylene	14
3.1	Designation of samples	67
4.1	Properties of manganese carboxylates	77
4.2	Losses of tensile properties of samples after 1000 hours of thermal treatment	87
4.3	Degradation temperatures of samples, before and after 1000 hours of thermal treatment	95
4.4	Melting temperatures and crystallinities of samples before and after 1000 hours of thermal treatment	97
4.5	Losses of tensile properties of samples after 1000 hours of accelerated weathering	107
4.6	Degradation temperatures of HDPE samples before and after 1000 hours of accelerated weathering	117
4.7	Melting temperatures of HDPE samples and their crystallinities, before and after 1000 hours of accelerated weathering	119
4.8	Comparison of crystallinities obtained from DSC scan and XRD trace before and after 1000 hours of accelerated weathering	121
4.9	Gambang average weather	123
4.10	Losses of tensile properties after 24 weeks of natural weathering	130
4.11	Degradation temperatures of HDPE samples before and after 24 weeks of natural weathering	139
4.12	Melting temperatures of HDPE samples and their crystallinities before and after 24 weeks of natural weathering	141
4.13	Comparison of crystallinities obtained from DSC scan and XRD trace before and after 24 weeks of natural weathering	142
4.14	Degradation temperatures and activation energies of selected samples before and after three different treatments	146
4.15	Melting properties of selected samples before and after three different treatments	147

LIST OF FIGURES

Figure No.	Title	Page
1.1	World plastics production 1950-2010	2
1.2	Plastics demand by converters 2010 in Europe: (a) breakdown by resin types, (b) breakdown by end use segments	2
1.3	Plastics demand in Malaysia 2010 breakdown by market segments of plastics products	3
2.1	Chemical structure of polyethylene	9
2.2	Molecular structure of polyethylene	10
2.3	Schematic of the molecular structure of different polyethylene (a) HDPE, (b) LDPE, and (c) LLDPE	12
2.4	The stress-strain behavior for brittle (curve A), plastics (curve B), and highly elastic (elastomeric) (curve C) polymers	22
2.5	Classification of thermogravimetry curves	32
2.6	Comparison TG curves and corresponding DTG curves	33
2.7	Temperature determination from a single-stage TG curve	33
2.8	Dependence of polymer properties as well as melting and glass transition temperatures on molecular weight	36
2.9	Schematic DSC curve for a polymeric sample	37
2.10	DTA curve of glass-ceramic sample	39
2.11	Polyolefin melting profiles	40
2.12	Plot of X-ray scattering intensity of linear-low density polyethylene	42
2.13	Three types of peak shapes in X-ray diffraction pattern (a) peak height proportional to peak area; (b) peak height not proportional to peak area; and (c) peak area overlapped by other peaks	43
2.14	Profile analysis of a diffractometer scan from polyethylene	44
2.15	Mechanism of thermo-oxidation of polyethylene	49
3.1	Flow chart of overall research	63
3.2	Dimension of specimen	69
4.1	TG traces of manganese carboxylates	77
4.2	DTG traces of manganese carboxylates	78
4.3	DSC scans of manganese carboxylates	79

4.4	FTIR spectra of ML10 samples, before (lower trace) and after (upper trace) thermal treatment	81
4.5	Carbonyl index of HDPE samples with various compositions during thermal treatment	82
4.6	Tensile strength of HDPE containing manganese laurate during thermal treatment	83
4.7	Tensile strength of HDPE containing manganese palmitate during thermal treatment	84
4.8	Tensile strength of HDPE containing manganese stearate during thermal treatment	84
4.9	Tensile modulus of HDPE containing manganese laurate during thermal treatment	86
4.10	Tensile modulus of HDPE containing manganese palmitate during thermal treatment	86
4.11	Tensile modulus of HDPE containing manganese stearate during thermal treatment	87
4.12	Elongation at break of HDPE containing manganese laurate during thermal treatment	88
4.13	Elongation at break of HDPE containing manganese palmitate during thermal treatment	89
4.14	Elongation at break of HDPE containing manganese stearate during thermal treatment	89
4.15	Average molecular weights of various samples during thermal treatment	91
4.16	MFI of various samples during thermal treatment	92
4.17	TG traces of pure samples, before and after 1000 hours of thermal treatment	93
4.18	DTG traces of pure samples, before and after 1000 hours of thermal treatment	94
4.19	TG traces of ML10 samples before and after 1000 hours of thermal treatment	94
4.20	DTG traces of ML10 samples, before and after 1000 hours of thermal treatment	95
4.21	Activation energy calculation for decomposition of pure sample	96
4.22	DSC scans of untreated and treated pure samples	97
4.23	DSC scans of untreated and treated ML10 samples	98
4.24	SEM image of samples (a) pure HDPE (b) ML10 (c) MP10 (d) MS10 before treatment	99
4.25	SEM image of samples (a) pure HDPE (b) ML10 (c) MP10	100

	(d) MS10 after 1000 hours of thermal treatment	
4.26	FTIR spectra of MP10 samples, before (lower trace) and after (upper trace) accelerated weathering	102
4.27	Carbonyl index of various samples during accelerated weathering	103
4.28	Tensile strength of HDPE containing manganese laurate during accelerated weathering	105
4.29	Tensile strength of HDPE containing manganese palmitate during accelerated weathering	105
4.30	Tensile strength of HDPE containing manganese stearate during accelerated weathering	106
4.31	Tensile modulus of HDPE containing manganese laurate during accelerated weathering	108
4.32	Tensile modulus of HDPE containing manganese palmitate during accelerated weathering	109
4.33	Tensile modulus of HDPE containing manganese stearate during accelerated weathering	109
4.34	Elongation at break of HDPE containing manganese laurate during accelerated weathering	110
4.35	Elongation at break of HDPE containing manganese palmitate during accelerated weathering	111
4.36	Elongation at break of HDPE containing manganese stearate during accelerated weathering	111
4.37	Molecular weight of various samples during accelerated weathering	113
4.38	MFI of samples during accelerated weathering	114
4.39	TG scans of pure samples before and after accelerated weathering	115
4.40	DTG scans of pure samples before and after accelerated weathering	116
4.41	TG scans of MP10 samples before and after accelerated weathering	116
4.42	DTG scans of MP10 samples before and after accelerated weathering	117
4.43	DSC scans of pure samples, before and after accelerated weathering	118
4.44	DSC scans of MP10 samples, before and after accelerated weathering	119
4.45	XRD traces of pure samples, before and after accelerated weathering	120

4.46	XRD traces of MP10 samples, before and after accelerated weathering	121
4.47	SEM image of samples (a) pure HDPE (b) ML10 (c) MP10 (d) MS10 after 1000 hours of accelerated weathering	122
4.48	FTIR spectra of MS10 samples before (lower trace) and after (upper trace) natural weathering	125
4.49	Carbonyl indexes of various samples during natural weathering	126
4.50	Tensile strength of HDPE containing manganese laurate during natural weathering treatment	128
4.51	Tensile strength of HDPE containing manganese palmitate during natural weathering treatment	129
4.52	Tensile strength of HDPE containing manganese stearate during natural weathering treatment	129
4.53	Tensile modulus of HDPE containing manganese laurate during natural weathering treatment	130
4.54	Tensile modulus of HDPE containing manganese palmitate during natural weathering treatment	131
4.55	Tensile modulus of HDPE containing manganese stearate during natural weathering treatment	131
4.56	Elongation at break of HDPE containing manganese laurate during natural weathering treatment	133
4.57	Elongation at break of HDPE containing manganese palmitate during natural weathering	134
4.58	Elongation at break of HDPE containing manganese stearate during natural weathering	134
4.59	Average molecular weight of samples during natural weathering	135
4.60	MFI of various samples during natural weathering	136
4.61	TG traces of pure samples, before and after 24 weeks of natural weathering	137
4.62	DTG traces of pure samples, before and after 24 weeks of natural weathering	138
4.63	TG traces of MS10 samples, before and after 24 weeks of natural weathering	138
4.64	DTG traces of MS10 samples, before and after 24 weeks of natural weathering	139
4.65	DSC scans of pure samples: before and after 24 weeks of natural weathering	140
4.66	DSC scans of MS10 samples: before and after 24 weeks of	141

	natural weathering	
4.67	XRD traces of pure samples before and after natural weathering	142
4.68	XRD traces of MS10 samples before and after natural weathering	142
4.69	SEM image of samples (a) pure HDPE (b) ML10 (c) MP10 (d) MS10 after 24 weeks of natural weathering	143
4.70	Comparison of CI after three different treatments	145
4.71	Comparison of losses of elongations at break after three different treatments	145
4.72	MW reductions after three different treatments	146
4.73	TGA traces of MS10 samples before and after three different treatments	147
4.74	DSC scans of MS10 samples before and after three different treatments	148

LIST OF SYMBOL

C	Concentration
E_a	Activation energy, kJ/mol
M_v	Average molecular weight
M_n	Number average
M_w	Weight average
$[\eta]$	Intrinsic viscosity
η_{sp}	Specific viscosity
η_{rel}	Relative viscosity
T_m	Melting temperature, °C
T_g	Glass transition temperature, °C
λ	Wave length of X-ray
d	Interplanar spacing of crystalline material
θ	Diffraction angle
ΔH_f	Heat of fusion, J/g
X_{DSC}	Crystallinity index obtained from DSC scan, %
X_{XRD}	Crystallinity index obtained from XRD trace, %

LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
COC	Cyclic olefin copolymer
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Differential thermogravimetry
FTIR	Fourier transform infrared
GPC	Gel Permeation Chromatography
HDPE	High density polyethylene
IR	Infrared
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MFI	Melt Flow Index
ML	Manganese laurate
MP	Manganese palmitate
MS	Manganese stearate
MW	Molecular weight
MWD	Molecular weight distribution
PC	Polycarbonate
PE	Polyethylene
PMMA	Polymethyl methacrylate
PS	Polystyrene
PVC	Polyvinyl chloride
SAN	Styrene acrylonitrile
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TG	Thermogravimetry
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Plastics have achieved almost irreplaceable role in many applications. Almost all aspects of life rely on the plastics. Recently, the usage of plastics increases significantly. Plastics have achieved an irreplaceable position in the packaging industry (Roy et al., 2006a). People rely to plastics in everyday activities, such as jugs, clothes, computer, etc (Bajer et al., 2007; Lokensgard, 2004). Plastics production systematically increases, thus, also amount of plastics waste grows (Bajer et al., 2007).

The world's annual production of polymer resins has experienced a steady growth since the beginning of the century, with growth predicted way into the 21st century. In developed countries, the growth in annual polymer production has diminished somewhat in recent years. However, developing countries in South America and Asia are now starting to experience tremendous growth (Osswald and Menges, 2003). From 2009 to 2010 the global plastics production increased by 15 million tonnes (6%) to 265 million tonnes, confirming the long term trend of plastics production growth of almost 5% per year over the past 20 years. Meanwhile in 2010 Europe accounted for 57 million tonnes (21.5%) of the global production and China overtook Europe as the biggest production region at 23.5% which mainly consisted of HDPE (11%), LDPE-LLDPE (17%), PP (18%) and PVC (8%). Figure 1.1 shows the growth of world plastics production from 1950-2010(PlasticsEurope, 2011).

There are over 18,000 different grades of polymers, available in the US alone. They can be divided into two general categories, thermosetting and thermoplastic polymers. In 1993, 90% of polymers produced in the United States were thermoplastics.

However, in a 1995 worldwide projection, thermoplastics account for 83% of the total polymer production (Osswald et al., 2006).

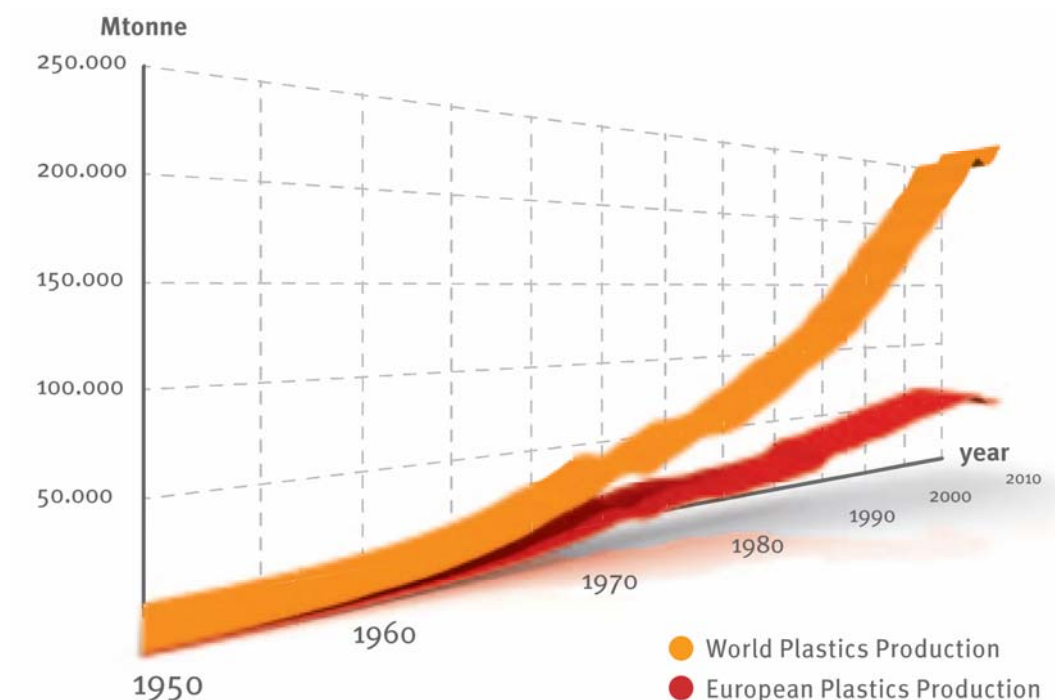


Figure 1.1 World plastics production 1950-2010 (PlasticsEurope, 2011)

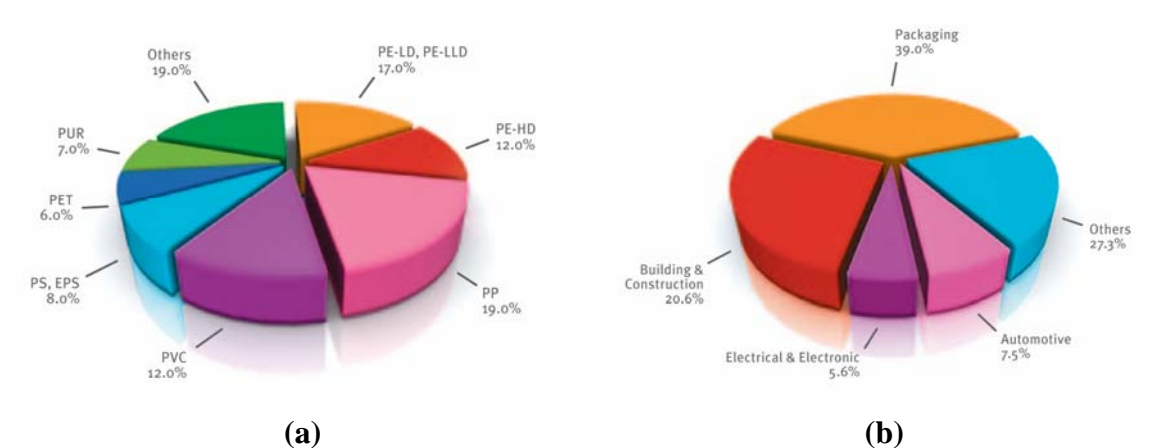


Figure 1.2 Plastics demand by converters 2010 in Europe: (a) breakdown by resin types, (b) breakdown by end use segments

There are five high-volume plastics families; polyethylene (including low density (LDPE), linear low density (LLDPE) and high density (HDPE)), polypropylene (PP), polyvinylchloride (PVC), polystyrene (solid PS and expandable EPS) and

polyethylene terephthalate (PET). Figure 1.2 shows plastics demand in Europe in 2010 (PlasticsEurope, 2011). Other data revealed that in 1999, the principal thermoplastic polymers (LDPE/HDPE, PP, PVC, PS, and PET) consumptions exceeded 28 millions tons in Western Europe, 79% of total plastic markets (thermoplastics and thermosets) in Western Europe and around 90% of total thermoplastics markets (Azapagic et al., 2003). In 2010 together the big five accounted for around 74% of all European plastics demands (PlasticsEurope, 2011).

In 2009 the total consumption of plastics resin in Malaysia accounted for 1.70 million metric tons (MT) (Boon, 2010). Previously total resin consumption accounted for 1.72 million MT in 2005, of which about 65% were polyolefins (PE & PP). Figure 1.3 represents the demand of plastics resin in Malaysia in 2005 by market segments. Packaging application accounted 36 % of total resin consumption (MPMA, 2005).

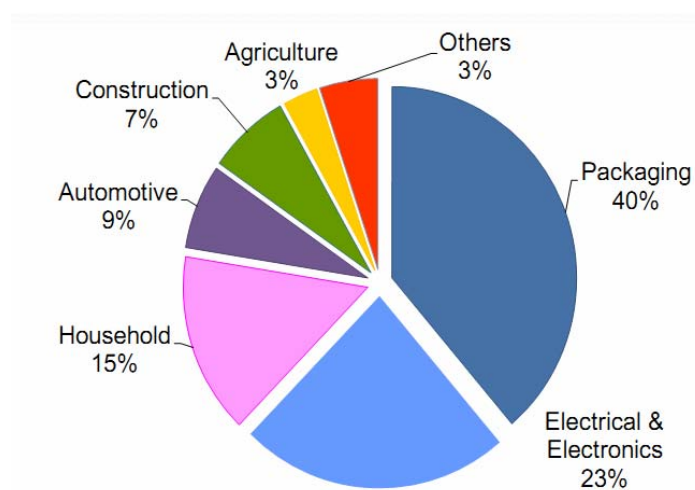


Figure 1.3 Plastics demand in Malaysia 2010 breakdown by market segments of plastics products.

Polyethylene is by far the most widely used polymeric material, accounting for 41% of the US plastic production (Osswald et al., 2006). Consumption of HDPE in United States was predicted that it would increase significantly (Lokensgard, 2004). In US, packaging accounts for over one-third of the captive use of thermoplastics, whereas construction, accounts for about half that number, and transportation account for only 4% of the total captive use of thermoplastics. On the other hand, 69% of the thermosets are used in building and construction, followed by used in transportation (Osswald and

Menges, 2003). Whereas in Europe, packaging remains the biggest end-use for plastics (40%) followed by electrical and electronic (23%), household (15%), automotive (9%), construction (7%), agriculture (3%) and others (3%) (PlasticsEurope, 2011).

Generally, most of packaging applications eventually end up as litter. Griffin (1993) reported that over 50% of the annual tonnages of all manufactured synthetic polymers are applied as packaging materials and that some 90% of this flow finishes as a component of urban garbage. The other report showed that the municipal solid waste stream in the U.S. totals nearly 160 metric tons per year and consists of about 7-11% by weight of post-consumer plastics (Andrady et al., 1993a). In 2001, plastics waste which mainly consisting of PE (above 40 wt %), PVC, PP, and poly-(ethylene terephthalate) had a total volume of 19.2 millions tons, accounting for about 8.4% of total municipal solid waste in the United States (Lei et al., 2007).

Plastic (polymers) is now being viewed as a serious worldwide environmental and health concern, especially for disposable application such as carrier and garbage bags. The increasing utilization of plastics has also caused concern for the role of plastics in environmental pollution (Lokensgard, 2004). Its character of being non-degradable is resulting in river pollution, choking in landfill, and is considered particularly undesirable and a hazard to animal life (Andrady et al., 1993a).

Some methods have been applied in order to reduce the effects of plastics on litter problem. In 1976, the Resource Conservation and Recovery Act (RCRA) promoted reuse, reduction, incineration, and recycling of materials. Recycling is a term generally reserved for post-consumer waste materials (Lokensgard, 2004). Most recycling programs accept plastics number 1 (PETE) and 2 (HDPE). The packaging of HDPE that appears in waste stream is only 25 percent of the total sales in 1993, 1,929,000 metric tons. The other products eventually find their way to landfills or incinerator (Lokensgard, 2004). However, the strategy of reduce, re-use, and recycling which have been introduced and applied widely, only overcome very small part of huge quantity of plastics waste.

1.2 PROBLEM STATEMENT

The growing environmental concern has made plastics a target of much criticism due to their lack of degradability (Albertsson et al., 1992). The large amounts of plastics ending up in the waste stream, has resulted in a trend towards manufacture and development of plastics with accelerated degradation time (Barr-Kumarakulasinghe, 1994).

Degradable polymers are designed to degrade in different ways and in different environments. An important distinction needs to be made between biodegradable plastics, i.e. those that capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms (bacteria, fungi, algae), and oxo-biodegradable plastics, which oxidize and embrittle in the environment and erode under the influence of ultraviolet (UV) light and heat (Excelplas, 2003).

The transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) could be considered for use in initiating degradation of polymers (Griffin, 1993; Osawa et al., 1979; Poyner and Cakraborty, 1993). Many studies mostly utilized cobalt-based additives for LDPE or LLDPE (Bikiaris et al., 1997; Roy et al., 2006a; Roy et al., 2007a; Roy et al., 2006b; Roy et al., 2007b; Roy et al., 2007c). The other studies utilized other transition metals, such as iron and calcium (Pablos et al., 2010) and manganese (Erlandsson et al., 1997; Khabbaz et al., 1999; Sharma et al., 2001) for LDPE. Manganese is close to cobalt in periodic table, having almost same atomic number with cobalt. Manganese is more available in the nature and cheaper than cobalt (Hartman, 1992). Moreover, most studies on degradation have focused on LDPE.

The study on effects of manganese carboxylates i.e. manganese laurate, manganese palmitate and manganese stearate on the degradation of HDPE during accelerated weathering and natural weathering under weather conditions of Gambang, Malaysia especially, and generally Peninsular Malaysia, hasn't been existed yet. Malaysia represents tropical area. In addition, HDPE is also widely applied for post consumer products, like: packaging, plastic mulch, bottle etc. However, only few studies on degradation have focused on HDPE due to its high crystallinity, therefore it is

more difficult to degrade than one with low crystallinity. This research studies the synthesis of manganese carboxylates and the effects of manganese carboxylates on the degradation of HDPE. This study also compares the performances of manganese carboxylates i.e manganese laurate, manganese palmitate and manganese stearate on accelerating degradation of HDPE under accelerated weathering and natural weathering under weather conditions of Gambang, Malaysia.

1.3 OBJECTIVE OF RESEARCH

This research has objectives as listed below:

1. To synthesize manganese carboxylates and study their characteristics
2. To investigate the characteristics of manganese carboxylates-HDPE blends.
3. To study the effects of manganese carboxylates in accelerating degradation of HDPE under thermal treatment
4. To study the effect of manganese carboxylates on the degradation of HDPE during accelerated weathering treatment.
5. To study degradation behavior of HDPE containing manganese carboxylates during natural weathering, particularly in Gambang, Malaysia

1.4 SCOPE OF RESEARCH

The scopes of this research consist of:

1. Synthesis of manganese carboxylates.
2. Characterization of manganese carboxylates.
3. Compounding of manganese carboxylates and HDPE resins.
4. Specimen molding (injection molding)
5. Investigate the effects of manganese carboxylates on properties of HDPE
6. Thermal treatment of HDPE containing manganese carboxylates and its effect on properties of HDPE.
7. Accelerated weathering of HDPE containing manganese carboxylates and its effect on properties of HDPE.
8. Natural weathering of HDPE containing manganese carboxylates and its effect on properties of HDPE.

1.5 CONTRIBUTION OF RESEARCH

The main outputs of this research are:

1. The synthesis methods of manganese carboxylates are developed.
2. Characterization of manganese carboxylates in terms of their physical and chemical properties is obtained.
3. The pro-degradant additives for degradable HDPE are proposed and developed.
4. Degradation rate of HDPE containing manganese carboxylates during thermal treatment is obtained.
5. Degradation behaviors of HDPE containing manganese laurate under accelerated weathering and natural weathering; particularly under weather conditions of Gambang, Malaysia are well-understood.
6. Reduce lifetime of plastics waste for better quality of environment.

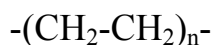
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION TO PLASTICS

Plastics are polymeric materials with properties that are between those of elastomers and fibers. Elastomers are giant molecules possessing what is referred to as memory that they can be deformed, misshaped, and stretched, and after applied stressing force is removed, they return to their original, pre-stressed shape. Fibers possess high tensile strength and high modulus (high stress for small strains, i.e. stiffness) related to a relatively high degree of crystallinity. Plastics exhibit some flexibility and hardness and varying degrees of crystallinity (Carraher Jr., 2003).

Polymers are very large molecules (macromolecules) that are comprised or built up of smaller units or monomers. This monomer term is also used to indicate the basic chemical compound from which the polymer is polymerized. For example, the polymer polyethylene is produced from the monomer ethylene. It is usual to represent such a polymer in terms of its chemical repeat unit, as follows:



where n , which is the number of repeating units, can be large (ASM International, 2003; Painter and Coleman, 1997).

Polymers can be placed into thermoplastic, thermoset, or elastomer category. Thermoplastics are those polymers that solidify as they cooled no longer allowing the long molecules to move freely. When heated, these materials regain the ability to flow, as the molecules are able to slide past each other with ease. Thermosetting polymers solidify by being chemically cured. Here, the long macromolecules cross-link with each other during cure, resulting in a network of molecules that cannot slide past each other.

The formation of these networks causes the materials to lose the ability to flow even after reheating. Compared to thermosets, elastomers are only lightly cross-linked which permits almost full extension of the molecules. However, the links across the molecules hinder them from sliding past each other, making even large deformations reversible. They are very soft and very compliant elastic materials (Osswald and Menges, 2003).

Thermoplastic polymers are divided into two classes: amorphous and semi-crystalline polymers. The most common semi-crystalline thermoplastics are high density polyethylene, low density polyethylene, polypropylene, polytetrafluoroethylene, polyamide (Carraher Jr., 2003; Osswald and Menges, 2003). Amorphous polymers form large group of materials, including glassy, brittle polymers (such as polystyrene (PS), polymethyl methacrylate (PMMA), styrene acrylonitrile (SAN), and cyclic olefin copolymer (COC)) and ductile polymers (such as polyvinyl chloride (PVC) and polycarbonate (PC)). The characteristic that such polymers have in common is their “amorphous” structure, which means that they do not exhibit any crystalline structure in X-ray or electron scattering experiments (Michler, 2008)

2.2 POLYETHYLENE

Polyethylene (PE) (sometimes known as polythene) was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant. Imperial Chemical Industries (ICI) (Vasile and Pascu, 2005). In its simplest form a polyethylene molecule consists of a long backbone of an even number of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon; chain ends are terminated by methyl groups. This structure is shown schematically in Figure 2.1 (Peacock, 2000), and the simple molecular structure is presented in Figure 2.2 (ASM International, 2003).

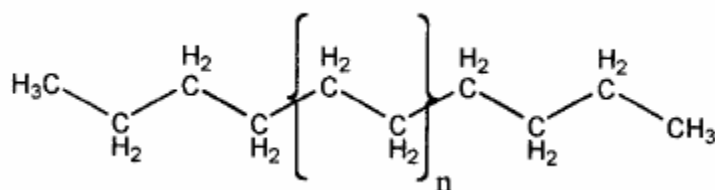


Figure 2.1 Chemical structure of polyethylene

Chemically pure polyethylene resins consist of alkanes with the formula $C_{2n}H_{4n+2}$, where n is the degree of polymerization, i.e. the number of ethylene monomers polymerized to form the chain. Unlike conventional organic materials, polyethylene does not consist of identical molecules. Polyethylene resins comprise chains with a range of backbone lengths. Typically the degree of polymerization is well in excess of 100 and can be as high as 250,000 or more, equating to molecular weights varying from 1400 to more than 3,500,000. Low molecular weight polyethylenes (oligomers) with a degree of polymerization between 8 and 100 are waxy solids that do not possess the properties generally associated with a plastic. When the degree of polymerization is less than 8, alkanes are gases or liquids at ordinary temperatures and pressures. Polyethylene molecules can be branched to various degrees and contain small amounts of unsaturation (Peacock, 2000).

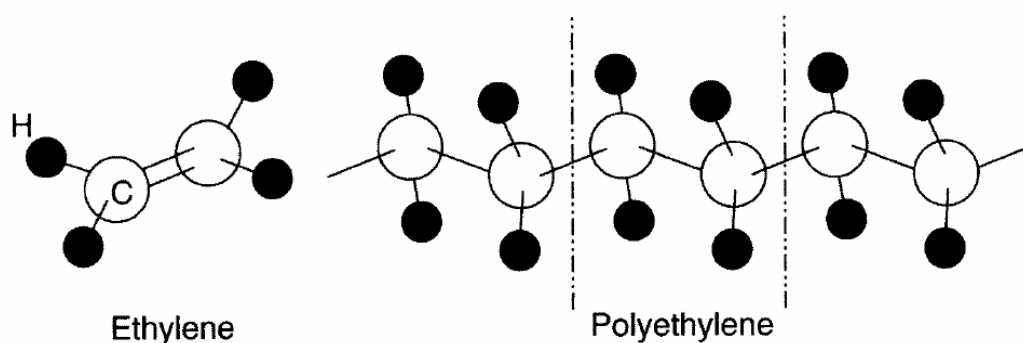


Figure 2.2 Molecular structure of polyethylene

Polyethylene is synthesized in several ways and resulting in different types of polyethylene. The branched polyethylene is called low density, high pressure polyethylene because of high pressure usually employed for its production; and because of the presence of the branches, the chains are not able to closely pack, leaving voids and subsequently producing a material that has a lower density in comparison to low-branched polyethylene. The other type of polyethylene is synthesized at much lower pressure and temperatures. This polyethylene has fewer branches and a higher softener temperature (above 100°C) (Carraher Jr., 2003).